Synthesis of a novel poly-thiolated magnetic nano-platform for heavy metal adsorption. Role of thiol and carboxyl functions

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ABSTRACT

We report a novel strategy for the synthesis of magnetic nano-platforms containing free thiol groups. It first involves the synthesis of a poly(acrylic acid) copolymer containing disulfide bridges between the linear chains through di-ester linkages, followed by the anchoring of this new ligand to magnetite nanoparticles using a ligand exchange reaction. Finally, free —SH groups are obtained by treating the resulting disulfide-functionalized magnetic nano-system with tributyl phosphine as reducing agent. The characterization of the resulting 17 nm nanoparticles (Fe_3O_4@PAA-HEDred) by FTIR and TGA confirms the attachment of the copolymer through iron carboxylates. XRD, TEM and magnetic measurements indicate an increase in the inorganic core diameter and the occurrence of strong magnetic inter-particle interactions during the exchange reaction, although coercitivity and remanence drop to near zero at room temperature. Afterwards, Fe_3O_4@PAA-HEDred nanoparticles were tested as sorbent for Pb^{2+} and Cd^{2+} cations in aqueous media. XPS measurements were performed in order to unravel the role of both carboxyl and thiol functions in the adsorption process. For the sake of comparison, the same study was performed using bare Fe_3O_4 nanoparticles and a nanosystem with disulfide groups (Fe_3O_4@DMSA). The joint analysis of the Pb 4f, Cd 3d, Fe 2p and S 2p high resolution spectra for the nanostructured materials indicates that metal-sulfur interactions are dominant if free —SH groups are present, but if not, the main adsorption route entails metal-carboxyl interactions. Even in presence of unbound thiol moieties, carboxyl groups participate due to favoured steric availability.

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1. Introduction

Magnetic ferrite nanoparticles are attracting great deal of attention in the recent past years, being one of the most active research fields in Nanoscience and Nanotechnology. Their magnetic properties [1,2], along with easy and cheap synthetic pathways [3], make them desirable materials for several biomedical [4], catalytic [5] and environmental applications [6], where removal of a target compound or material from a complex matrix can be achieved by means of an external magnetic field. Magnetite (Fe_3O_4) is specially employed in adsorption strategies for heavy metals [6,7], since it has no toxicity for living organisms and its surface offers great versatility [8] in order to functionalize the nanoparticles with the proper ligand that binds the target contaminant. In this sense, amino, carboxyl and thiol chemical groups play important roles for cation incorporation into the adsorbing material, depending on the hardness of the cation to be adsorbed through coordination [9]. Heavy metals are one of the most widespread and dangerous family of hazardous materials that can be encountered in natural and waste waters due to the increasing development of industrial processes; many of them are not self-degradable and can be accumulated in living organisms, being responsible for serious diseases that affect human health even at low concentrations [10]. Among the numerous strategies that have been developed to eliminate heavy metal cations from aqueous media [11–13], adsorption methodologies have proved to be more efficient, practical and economic than others [14,15].

Thiol-containing ligands for iron oxide nanoparticles have focused the attention of several research groups. Cysteine [16], and specially m-2,3,dimercapto succinic acid (DMSA) [17,18] have been employed for a wide variety of biological applications, owing to its excellent biocompatibility [19,20]. Besides, several magnetic platforms decorated with thiol moieties have been tested for adsorption of heavy metal cations [21–24], provided the high affinity of −SH groups to soft Lewis acids. Recently, considerable research has been devoted to macromolecular thiolated ligands [25–28] in order to increase the efficiency and robustness of the adsorbing nanomaterials. Nevertheless, direct use of free thiols during magnetite functionalization presents some drawbacks. It seems that extensive disulfide formation decreases the amount of −SH moieties [29]; at the same time, it cannot be excluded the fact that magnetite phase is altered as a result of thiol oxidation [30], which is reflected in a lower value of the saturation magnetization.

In a pioneer paper, Yantasee et al. [31] reported the adsorption of several heavy metal cations onto Fe_3O_4@DMSA nanoparticles; however, the roles of both carboxyl and thiol functions in the adsorption process were not clear. After that, a report from our group [32] suggested that for Au(III) adsorption onto the same nano-system, thiol oxidation is not a drawback, since this cation is mainly incorporated to the nanoparticles by reduction and adsorption as Au^0 in presence of disulfide groups, while Au (III) coordination to carboxyl moieties plays a secondary role. Hence, the actual metal coordination mode and the influence of the sulfur chemical state for the case of non-reducible metal cations remain as open questions. Our hypothesis is that if the adsorption of non-reducible cations (e.g. Pb^{2+} and Cd^{2+}) as metal sulfides is desired, the occurrence of free −SH groups at the nano-adsorbent surface must be mandatory.

With this in mind, herein we report the synthesis and characterization of a new carboxyl and thiol-based magnetic nano-platform named Fe_3O_4@PAA-HEDred. Besides, the interactions of this nano-adsorbent with Pb(II) and Cd(II) cations are studied by means of X-ray Photoelectron Spectroscopy (XPS) technique. This novel nano-system entails magnetite nanoparticles as magnetic core, which are functionalized with a copolymer derived from poly(acrylic acid) that contains free −SH and −COOH groups. First, it is synthesized a polymeric ligand, poly(acrylic acid)-hydroxyethyl disulfide (PAA-HED), bearing multiple carboxylic groups and disulfide moieties as protected thiol groups; then, we proceeded to magnetite functionalization. With this strategy, it is possible to obtain a magnetic nano-platform (Fe_3O_4@PAA-HED) with latent −SH functions that could be liberated by reduction, to form PAA-HEDred, just before the cations adsorption tests. Such strategy for thiol protection constitutes an alternative methodology to that proposed earlier by Maurizi et al. [33], which involved the grafting of poly(ethylene glycol) chains onto the oxide surface in order to avoid the formation of intermolecular disulfide bridges by steric hindrance. Finally, in order to shed light over the role of both carboxyl and thiol groups, XPS studies also include the interactions between Pb(II) and magnetite nanoparticles either without capping ligand (Fe_3O_4) or capped with DMSA molecules (Fe_3O_4@DMSA), in which −SH groups are mostly converted to −S−S− bridges.

2. Experimental

2.1. Materials and equipment

All reactants were purchased from Sigma Aldrich and, unless stated, were used without further purification. The water employed was bidistilled. Synthesis and characterization of oleic acid coated magnetite nanoparticles (Fe_3O_4@OA) employed in Section 2.5 can be found in Appendix A of Supporting material. Fe_3O_4 and

Fe_3O_4@DMSA nanoparticles used as model sorbents for XPS studies were synthesized and characterized according to a previously published paper [32].

IR spectra were recorded in transmission mode with a Perkin Elmer Spectrum One spectrometer by diluting the samples in pressed disks of KBr. Thermogravimetric analyses were performed in High Resolution TGA Q5000 IR equipment at heating rate of $10\,^\circ$C/min under a continuous nitrogen flow. The XRD powder patterns were recorded at room conditions using a D8 Advance diffractometer (from Bruker) and $CuK\alpha_1$ radiation. The UV–vis spectra were recorded at room temperature in the 300–800 nm wavelength range using a Cary spectrophotometer and placing samples in quartz cuvettes (1 cm path length). 1D and 2D NMR measurements were performed in liquid mode with a Bruker Ascend spectrometer at 750 MHz as working frequency; samples were dissolved in DMSO-d_6. Elemental analysis was done with a Perkin Elmer 2400 Series II CHNS/O analyser coupled with an AD-6 ultra-microbalance.

Magnetic data were collected in the 2–300 K temperature range using an MPMS-5 SQUID. Zero Field Cooling (ZFC) and Field Cooling (FC) curves were recorded at 50 Oe, while the sample temperature was varied at a rate of 1 K/min, both on heating and on cooling. For isothermal magnetization loops, the applied magnetic field was varied from −20 to 20 kOe. Samples for electron microscopy were initially suspended in ethanol followed by deposition of a drop onto a carbon-coated copper grid of 200 meshes. After evaporation of the solvent, the particles were analysed by Transmission Electron Microscopy (TEM JEOL JEM 1010) and High Resolution (HRTEM JEOL 2010F), using accelerating voltages of 60 kV and 200 kV, respectively. For Fe_3O_4@OA sample, hexane was used as solvent.

XPS analyses were performed using a Thermo Scientific K-Alpha X-ray photoelectron spectrometer with a monochromatic Al_K X-ray source (1487 eV) and a base pressure of 1×10^{-9} Torr in the analytical chamber. The position of the adventitious carbon C 1s peak at 284.8 eV was monitored on each sample to ensure that no binding energy shift due to charging had occurred. Survey scans were recorded using 400 μm spot size and fixed pass energy of 160 eV, whereas narrow scans were collected at 60 eV analyser pass energy. High resolution spectra were deconvoluted by using the Shirley model as background and a mixture 70%–30% of Gaussian-Lorentzian contributions for line-shapes.

2.2. Synthesis of PAA-HED and PAA-HEDred

In a round bottom flask, 0.4 g (5.56 mmol of −COOH groups) of poly(acrylic acid) (PAA, $M_W \sim 1800$ Da), 170 μL (1.39 mmol, equivalent to 2.78 mmol of −OH groups) of 2-hydroxyethyl disulfide (HED) and 34 mg (0.278 mmol) of 4-dimethyl aminopyridine (DMAP) are dissolved in 15 mL of DMF. The solution is placed in an ice bath at $0\,^\circ$C. Separately, 0.533 g (2.78 mmol) of 1-ethyl-3-(3-dimethyl-aminopropyl) carbodiimide hydrochloride (EDC.HCl) are dissolved in 15 mL of DMF. This last solution is poured slowly into the first one through a dropping funnel under magnetic agitation. After 30 min, the ice bath is removed and the reaction is left for 24 h. The resulting solution is then precipitated with a ten-fold excess (v/v) of a 1 M HCl solution saturated with NaCl; a fine white powder was obtained. This solid is washed several times with fresh 1 M HCl solution and pure water. Finally, it was dried under vacuum at $50\,^\circ$C with $CaCl_2$ as desiccant overnight. The process is depicted is the left side of Scheme 1.

The resulting disulfide copolymer of PAA was further subjected to reduction with tributyl phosphine (Bu_3P). Briefly, 50 mg (71 μmol of disulfide) of PAA-HED were dissolved in 5 mL of DMF. To this solution 100 μL of water and 35 μL (140 μmol) of Bu_3P were added. The reaction mixture was sealed and stirred magnetically for